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A rationally designed perfluorinated host for the extraction of PFOA from water utilising non-covalent interactions

Harrison Omorodion^a, Miguel Palenzuela^a, Manuel Ruether^a, Brendan Twamley^a James A. Platts^b and Robert J. Baker^{*a}

Perfluorooctanoic acid (PFOA) is a persistent organic pollutant and widespread in the environment. Three hosts have been synthesized based upon the formation of a fluororous cavity and hydrogen bonding receptors with the aim of extracting PFOA from water into organic solvents. The hosts based upon a calix[4]arene functionalized at the lower rim with amide groups and fluororous ponytails are effective for the quantitative removal of PFOA. A modification to the partial cone or a trisaminoamine framework reduce the conformational rigidity and lowers the extraction efficiency. A comprehensive NMR spectroscopic analysis both in solution and the solid state, along with other characterization techniques have elucidated the stoichiometry of the host:guest species and the binding constants have been measured. A computational study has given further insight into the binding modes and corroborated the spectroscopic measurements.

Introduction

Perfluorinated compounds have a multitude of uses, partly due to their unique hydrophobic and lipophobic character. In the past 60 years, they have been used as stain, grease and water repellents or in the manufacture of products as diverse as paints to polishes, adhesives and firefighting foams.¹ However, due to the very strong C—F bond (485 kJ mol⁻¹) recent concern over the toxicity² and bioaccumulation³ has forced the reclassification as persistent organic pollutants (POPs).⁴ One of the major pollutants is perfluorooctanoic acid (PFOA), which has been found in oceans⁵ and rivers⁶ across the world, in the blood serum of numerous animal species,⁷ occupationally exposed⁸ workers and the general public.⁹ Perfluorinated compounds are ubiquitous in the Arctic regions,¹⁰ which points to complex transport mechanisms,¹¹ and indicates these POPs are globally distributed, with some evidence of vaporization of neutral PFOA from water.¹² The probable source of PFOA and related compounds are thought to be from fluorinated alcoholic telomers, although this has been the subject of robust debate.¹³ In the context of an environmental pollutant, it is not treated by current waste water technologies so can contaminate drinking water supplies.¹⁴ As the C-F bond is very strong, selective dehydrofluorination methodologies based on transition metal catalysts have not been used to a great extent,¹⁵ but recent results with non-metals may hold promise.¹⁶ More traditional

methods such as sorption¹⁷ onto activated carbon,¹⁸ polyaniline nanotubes,¹⁹ carbon nanomaterials,²⁰ and photo-degradation²¹ especially using Ga₂O₃,²² In₂O₃,²³ Fe(III)²⁴ and modified TiO₂²⁵ catalysts have been reported. Reaction with

•OH radicals is not very efficient for photo-degradation, but Fenton-like chemistry using H₂O₂ has been reported.²⁶ Persulfate oxidation under UV-conditions is also reported to be efficient.²⁷ Coagulation techniques,²⁸ ball milling,²⁹ γ-irradiation³⁰ and sonochemistry³¹ have also been utilized in this field, but conspicuous in its absence is a solvent extraction process.

We have an interest in the synthesis of fluororous ligands and have shown that some of these are useful for the extraction of toxic metals from water.³² On the basis of structural and theoretical investigations we have recently shown that C—F...F—C interactions are stabilizing in the solid state, and collectively can add the same amount of stabilizing energy as a hydrogen bond.³³ There are now a growing number of examples of F...F interactions being utilized as crystal engineering for applications in materials chemistry³⁴ or in catalysis.³⁵ Interest in weak C—H...F—C bonding is also burgeoning.³⁶ Bearing in mind the extensive use of non-covalent interactions in sensing anions,³⁷ we reasoned that with a suitably designed ligand we could extract PFOA from aqueous media, thus offering a remediation strategy. For this aim to be realized a number of features need to be incorporated into the ligand system. A conformationally rigid ligand would be thermodynamically favorable in forming stable host-guest complexes; a system based on a calix[4]arene would be useful as this has been used prodigiously in supramolecular chemistry.³⁸ Hydrogen bonding will be the primary non-covalent interaction,³⁹ and to increase the propensity for this to occur, electron withdrawing groups

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near the donor atoms are required.⁴⁰ Whilst for the highly electron-withdrawing fluororous ponytails eight methylene units are required for full insulation,⁴¹ in practice two is almost as effective. It is also known that the fluororous acid is a strong acid, so hydrogen bonding strategies using both of these inductive effects have been described.⁴² It should be noted that the measurement of pKa's has been controversial, with a range <0.1–3.8 reported, depending upon the conditions of the measurement and the concentration of PFOA.⁴³ "Dipole engineering"⁴⁴ also lends itself to this topic as adding a fluororous chain reverses the dipole compared to a hydrocarbon framework that can then match the dipole of the fluororous acid. Furthermore the presence of a long fluororous chain on the host will also allow a fluorophilic cavity to engender F...F interactions and add a further stabilizing non-covalent interaction. It should be noted that host-guest complexes with PFOA and its derivatives has not been studied in detail, although some success has been seen with cyclodextrin hosts⁴⁵ and a tripodal fluororous amide⁴⁶ has been used to form host-guest complexes with the related perfluorooctane sulfonate (Chart 1). Here we report on the synthesis of three types of hosts of varying conformational flexibility based upon a calix[4]arene or tren framework, and their reactivity with PFOA as characterized by thermal methods, vibrational spectroscopy and multinuclear NMR spectroscopy, both in solution and the solid state. We also show that these hosts can extract PFOA from water into an organic solvent with excellent efficiencies, thereby offering a new remediation technique for the removal of a persistent organic pollutant.

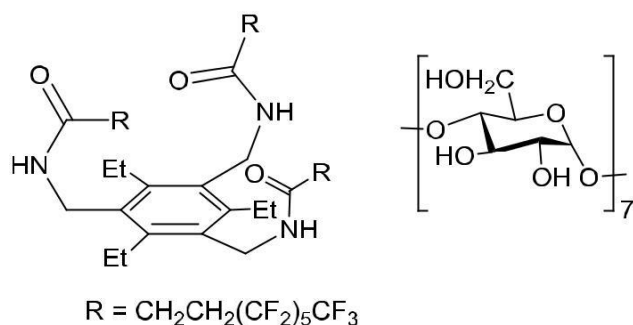


Chart 1. Examples of host-guest complexes.^{46,47}

Experimental

¹H, ¹³C{¹H} and ¹⁹F NMR solution spectra were recorded on a Bruker AV400 spectrometer operating at 400.23 MHz, 100.61 MHz and 376.55 MHz respectively, and were referenced to the residual ¹H and ¹³C resonances of the solvent used or external CFCl₃. Solid state NMR spectra were recorded on a Bruker 400 HD at 100.61 MHz (¹³C), 376.50 MHz (¹⁹F). IR spectra were recorded on a Perkin Elmer Spectrum One spectrometer with attenuated total reflectance (ATR) accessory. Mass spectra were measured on a MALDI QTOF Premier MS system. DSC spectra were recorded on a Perkin Elmer Diamond DSC and

TGA on a Perkin Elmer Pyris 1 TGA. All spectrophotometric analysis were measured on a Lambda 1050 UV-Vis NIR, using fused silica cells with a path length of 1 cm. X-ray crystallography data were measured on a Bruker Apex diffractometer. The structure was solved by direct methods and refined by least squares method on F² using the SHELXTL program package.⁴⁸ Crystal data for C₈H₁₅O₂ (M = 414.09 g/mol): triclinic, space group P-1, a = 9.9639(17) Å, b = 10.7932(18) Å, c = 23.575(4) Å, α = 9.9639(17)°, β = 90.839(4)°,

γ = 90.018(4)°, V = 2518.0(7) Å³, Z = 8, T = 100 K, μ(MoKα) = 0.296 mm⁻¹, D_{calc} = 2.185 g/cm³, 25077 reflections measured (0.870° ≤ θ ≤ 25.499°), 9338 unique (R_{int} = 0.0630) which were used in all calculations. The final R₁ was 0.0971 (I > 2σ(I)) and wR₂ was 0.2831 (all data). The structure was refined as a 2 component rotational twin (twin law: -1 -0.001 0 0 1 0 0 -0.505 -1) with a refined fractional twin volume of 19.78%. The structure was refined with restraints (RIGU, ISOR) and to convergence. The high residuals may be twinning artefacts. CCDC 1530103 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

All compounds and solvents were obtained from commercial sources and used as received. The synthesis of **1** and its conversion to **3** has been reported in the literature, and the spectroscopic data in our hands are in accord with this.⁴⁹ The transition of **2** to **4** has not been reported previously. The

CF₃(CF₂)₅CH₂CH₂NH₂ acid⁵⁰ CF₃(CF₂)₅CH₂CH₂CO₂H and the

were prepared via the literature. Spectroscopic data are collated in the supporting information (Figures S1-S16).

2,2',2'',2'''-((15,35,55,75-tetra-tert-butyl-1,3,5(1,3)-tribenzene-7(1,3)-cyclohexanacyclooctaphane-73,75-diene-12,32,52,72-tetrayl)tetrakis(oxy))tetraacetic acid, 2

A solution of NaOH (4.00 g, 100 mmol) in ethanol (60 cm³) and H₂O (40 cm³) was added to 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetracarboxymethoxycalix[4]arene (6 g, 6 mmol) and refluxed for 24 h. The cooled solution was acidified with 50% sulfuric acid to pH 1 and the resulting precipitate was isolated and dissolved (partially soluble) in ethanol-water (1:1 v/v) for recrystallization yielding **1** as colourless needles. The undissolved precipitate was collected, washed with water and dried at 40 °C to afford the pure **2** (5g, 94%). Spectroscopic data of **1** are in accord with the literature.⁵² IR $\tilde{\nu}$ (cm⁻¹) = 3610 (b, OH), 2994 (m, C-H), 1730 (s, C=O, carboxylic acid), 1479 (m, C-H), 1392 (w), 1362 1259 (w, C-H), 1191, 1127, 1053 (s, C-O),

870 (m, C-H), 800, 753 (s, C-H), 634 (w, C-H). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.04 (s, OH); 7.13, 7.19, 6.64, 6.60 (s each, 2 H each, ArH); 4.54 (br, 8 H, ArOCH₂); 4.41, 3.47 and 3.34 (d, 2 H, 4 H, J = 13 Hz, ArCHAr); 1.35, 1.28 and 0.89 (s, 18 H, ^tBu).

¹³C{¹H} NMR (400MHz, CDCl₃) δ (ppm) 149.9 (COOH); 125.7

(ArC), 53.2 (ArOC), 30.0 (CH₃); 31.0 (ArCH₂Ar). MS (MALDI) m/z: 880.4398 [M+Na, 100%]; HRMS (MALDI) calculated for C₅₂H₆₄O₁₂Na: 903.4295 Found: 903.4299.

2,2',2'',2'''-((15,35,55,75-tetra-tert-butyl-1,3,5(1,3)-tribenzena-7(1,3)-cyclohexanacyclooctaphane-73,75-diene-12,32,52,72-tetrayl)tetrakis(oxy))tetraacetyl chloride, 4

The acid **2** (2 g, 2 mmol) was refluxed with excess SOCl₂ under Argon at 120 °C for 6 h. The excess SOCl₂ was removed under reduced pressure to afford **4** which was verified by IR spectroscopy and used without further purification. IR $\tilde{\nu}$ (cm⁻¹) = 2962 (m, C-H), 1808 (s, C=O, acetyl chloride), 1477 (m, C-H), 1415 (w), 1362 1333 (w, C-H), 1259, 1192, 1062 (s, C-O), 948, 805, 758 (s, C-H), 691 (w, C-H).

[2,2',2'',2'''-((15,35,55,75-tetra-tert-butyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-12,32,52,72-tetrayl)tetrakis(oxy))tetrakis(N-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)acetamide)], 5

1-amino-1H,1H,2H,2H-perfluorooctane (1.6 g, 4.4 mmol) was added to a solution of tetraacetyl chloride, **3** (0.8 g, 0.80 mmol) dissolved in THF. Et₃N (10 cm³) was added to the reaction mixture and refluxed for 24 h. The solvent was removed *in vacuo* and the brown solid was taken up in DCM (80 cm³) and washed with H₂O (3 x 60 cm³), dilute HCl (3 x 60 cm³) and brine (60 cm³). The combined organic phases was dried with MgSO₄, and the solvent was removed under reduced pressure to obtain the crude brown solid which was purified by column chromatography (hexane/ethyl acetate, 5:2) to afford **5**. Yield 1.3 g, (67%). IR $\tilde{\nu}$ (cm⁻¹) 3210 (b, N-H), 2970 (w, C-H), 1668 (s, C=O, Amide), 1480 (s, C-H), 1365 (s, C-N), 1233, 1189, 1143, 1121 (s, C-F), 1075, 1016 (w, C-F), 803 (m, C-N), 732, 707 (m, C-H), 696 (m, C-H). ¹H NMR (CDCl₃) δ (ppm) 7.71 (s, 4 H, NH); 6.82 (s, 8 H, ArH); 4.9 (s, 8 H, ArOCH₂); 4.44, 3.28 (s, 8H, ArCHAr); 3.56 (t, 8 H, J = 7 Hz, NHCH₂); 2.43 (m, 8H, CH₂CF₂); 1.12 (s, 36 H, CH₃). ¹³C{¹H} NMR (CDCl₃) δ (ppm) 170 (OCNH); 152, 148 (ArC); 134-111 (CF); 74 (ArOC); 36.8 (ArCH₂Ar); 34.0 (CNH); 30.4 (CH₃); 29.8 (CCF₂). ¹⁹F NMR (CDCl₃) δ (ppm) -80.79 (s, CF₃); -113.89 (s, CF₂CH₂); -121.68 (s, CF₂); -122.68 (s, CF₂); -123.24 (s, CF₂); -125.98 (s, CF₂). MS (MALDI) m/z: 2260.5146 [M+Na, 100%]; HRMS (MALDI) calculated for C₈₄H₈₀N₄O₈F₅₂Na: 2283.5044, found 2283.5063.

2,2',2'',2'''-((15,35,55,75-tetra-tert-butyl-1,3,5(1,3)-tribenzena-7(1,3)-cyclohexanacyclooctaphane-73,75-diene-12,32,52,72-tetrayl)tetrakis(N-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)acetamide)], 6

1-amino-1H,1H,2H,2H-perfluorooctane (3 g, 8 mmol) was added to a stirred solution of **4** (2 g, 2 mmol) in the THF (80 cm³). Et₃N (10 cm³) was added to the reaction mixture and refluxed for 24 h. The solvent was removed *in vacuo* and

extracted with DCM (3 x 60 cm³). The organic phase was washed with H₂O (3 x 60 cm³), dilute HCl (3 x 60 cm³) and brine (60 cm³). The combined organic phases was dried with MgSO₄, and the solvent was removed under reduced pressure to obtain the crude brown solid which was purified by column chromatography (hexane/ethyl acetate, 5:2) to afford **6** as a brown solid. Yield 1.3 g, (67%). IR $\tilde{\nu}$ (cm⁻¹) 3210 (b, N-H), 2970 (w, C-H), 1668 (s, C=O, Amide), 1480 (s, C-H), 1365 (s, C-N), 1233, 1189, 1143, 1121 (s, C-F), 1075, 1016 (w, C-F), 803 (m, C-N), 732, 707 (m, C-H), 696 (m, C-H). ¹H NMR (CDCl₃) δ (ppm) 8.6, 8.24, 7.9, (bs, 4 H, NH); 7.03, 6.97, 6.86, 6.64 (s, 8 H, ArH);

4.82, 4.60, 4.49 and 4.45 (s, 4 H, ArOCH₂); 4.39, 3.29 (d, 8 H, ArCH₂Ar); 3.70 (m, 8 H, OCH₂CH₂); 2.45 (m, 8 H, CH₂CF₂); 1.35, 1.28, 1.09 and 0.89 (m, 36 H, ^{tBu}). ¹³C{¹H} NMR (CDCl₃) δ (ppm) 169.0 (CO₂NH); 146, 133, 130, 128, 125 (ArC), 120.4, 118.2, 116.8, 115.3, 110.2, 107.9, (CF₂ and CF₃) 65.4, 61.8, 57.8 (ArOC); 38.1 (ArCH₂Ar); 33.2 (CH₂NH); 32.01 (CH₂CF₂); 31.5, 29.9 (CH₃). ¹⁹F NMR (CDCl₃) δ (ppm) -80.79 (s, CF₃); -113.89 (s, CF₂CH₂); -121.68 (s, CF₂); -122.68 (s, CF₂); -123.24 (s, CF₂); -125.98 (s, CF₂). MS (MALDI) m/z: 2260.5146 [M+Na, 100%]; HRMS (MALDI) calculated for C₈₄H₈₀N₄O₈F₅₂Na: 2283.5044, found 2283.5132.

2H,2H-perfluorooctanoyl chloride, 7

2H,2H-perfluorooctanoic acid (0.70g, 1.8 mmol) was refluxed with freshly distilled thionyl chloride (1 cm³) for 40 h. The excess thionyl chloride along with the HCl and SO₂ gases produced were evaporated under reduced pressure. IR $\tilde{\nu}$ (cm⁻¹) = 2963 (w, C-H), 1807 (s, C=O, Acetyl chloride), 1681 (s, C=C), 1363, 1388, 1317 (w, C-H), 1232, 1186, 1142, 1121 (s, C-F), 1068, 1077 (w, C-F), 979, 897, 848, 810, 708 (w, C-H), 628, 614 (m, C-H).

N,N',N''-(nitritotris(ethane-2,1-diyl))tris(3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamide), 8

7 (0.4 g, 2.4 mmol) was refluxed with triethylamine (0.15 cm³, 1 mmol) and tris-(2-aminoethyl)-amine (0.13 g, 0.8 mmol) in THF (10 cm³) for 24 h and then diluted with 0.1 M HCl (20 cm³). The product was extracted with ether (3 x10 cm³) and saturated aqueous NaHCO₃ (10 cm³) was added. The combined ether extracts were dried over Na₂SO₄ and concentrated to obtain the syrupy crude product which was purified by column chromatography (Hexane/ethyl acetate, 5:1) to afford **8** as a

brown viscous liquid. (0.7 g, 57%). IR $\tilde{\nu}$ (cm⁻¹) 3253 (b, N-H), 2962 (w, C-H), 1638 (s, C=O, Amide), 1461 (s, C-H), 1353 (s, C-N), 1231, 1195, 1140, 1112 (s, C-F), 1085, 1061 (w, C-F), 863

(m, C-N), 805, 746, 721, 708 (m, C-H), 643 (m, C-H). ¹H NMR [600 MHz, C₂D₆CO]: δ (ppm) 8.03 (s, 3 H, HN); 3.34 (m, 6H, CH₂NHCO); 2.65 (m, 12 H, NCH₂CH₂ and CH₂CF₂ overlap).

¹³C{¹H} NMR [600 MHz, C₂D₆CO]: δ 166.6 (, NCO); 118.7 (m, CF₂); 117.8 (m, CF₂CF₂CH₂); 116.9 (m, CF₂CF₂CH₂); 111.7 (m,

CF₃CF₂CF₂CF₂); 110.9 (m, CF₃CF₂CF₂); 109.9 (m, CF₃CF₂); 82 (CH₂N); 55 (CH₂NHCO); 39.8 (CH₂). ¹⁹F NMR [376.6 MHz, C₆D₆]: δ -81.9 (s, CF₃); -119.07, 119.75 (s, CF₂CH₂); 123.22, -123.59 (s, CF₂CF₂); -126.1 (CF₃CF₂). MS (ESI-) m/z: 1226.0991 [M+H, 100%]; HRMS (ESI+) calculated for C₃₀H₂₂N₄O₃F₃₉: 1227.1069, found: 1227.1074.

General Procedure for the Extraction of PFOA: The ligands (1 molar equivalent) were dissolved in 1,3-bis(trifluoromethyl)benzene (5 cm³). Solutions of PFOA (1.8 mg, 0.004 mmol) in distilled H₂O (5 cm³) were carefully added to the ligand solutions and stirred. The concentration of PFOA in the aqueous layer was periodically monitored spectrophotometrically using the peak at 206 nm and referenced to a standard curve. Control experiments were carried out without the ligands.

General procedure for synthesis of host:guest complexes:

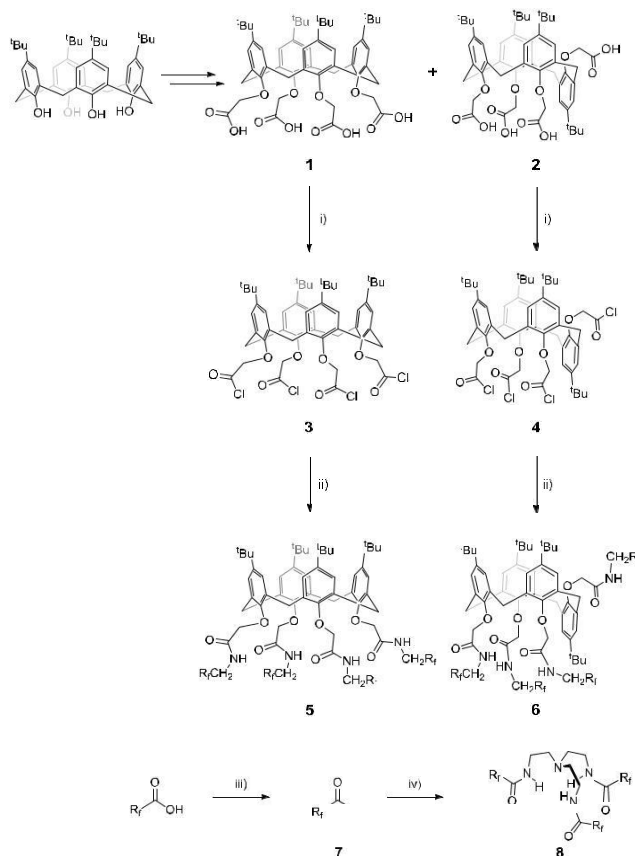
The hosts (25.0 mg, 0.02 mmol for **8**; 25.0 mg, 11 mmol for **5** and **6**) were dissolved in isopropanol (5 cm³) and added to a 1 and 2 molar equivalents of PFOA (3.3 mg and 6.7 mg for the **8**; 4.8 mg and 9.8 mg for the **5** and **6**) dissolved in H₂O (5 cm³).

The solution were stirred at 80 °C for 1 hr and then at 50 °C to completely evaporate all solvents.

Results and Discussion

Ligand synthesis and structure. The syntheses of the three ligands we have chosen to study are shown in Scheme 1. Whilst **1** and **3** are known compounds we found that under our experimental conditions 66% of the ‘partial-cone’ conformer **2** was formed.⁵³ We subsequently optimized the synthetic conditions to form **1** or **2** cleanly and in good yield. The conversion to the acid chloride is straightforward and reaction with the fluororous amine CF₃(CF₂)₅CH₂CH₂NH₂ allowed a high yielding synthesis of both full (**5**) and partial-cone (**6**) calix[4]arene with substituted amide groups on the lower rim. The synthesis of **8** was straightforward. The spectroscopic data of **5**, **6**, and **8** are in accord with our formulations but despite repeated attempts, no crystals suitable for single crystal X-ray diffraction could be isolated. The NMR and vibrational data of the hosts are discussed further in the host-guest section below.

During the course of a reaction between CF₃(CF₂)₆CF₂I and NaN₃ in DMF, instead of isolating the expected CF₃(CF₂)₆CF₂N₃, a colorless, crystalline product was formed that was shown to be CF₃(CF₂)₆CO₂H, PFOA, by X-ray diffraction. The mechanism of formation is not clear but careful analysis of the crude mixture by NMR spectroscopy shows this to be the only product. Dissolution of CF₃(CF₂)₅CH₂CH₂I in DMF has been reported to afford a number of products,⁵⁴ and perhaps given the electron withdrawing nature of the fluororous chain this weakens the C-I bond and is thus more reactive with DMF.



Scheme 1. Synthesis of hosts **5**, **6** and **8**. i) SOCl₂; ii) R_fNH₂; iii) SOCl₂; iv) tren, Et₃N. R_f = CF₃(CF₂)₅CH₂.

Interestingly, we have not been able to obtain single crystals from recrystallizing commercially available PFOA, and to the best of our knowledge this is the first time that PFOA has been structurally characterized. It should be noted that the crystals were twinned and were modelled as such. Nevertheless, the structure of PFOA and its packing along the b-axis are shown in Figure 1. The C-F bond lengths range from 1.309(14) – 1.371(10) Å, whilst the C-C bonds are between 1.510(16) -

1.576(14) Å. The commonly observed twisting of the chain is also observed so that the F—C—F torsion angles are lower compared to hydrocarbon chains. This is to relieve electrostatic interactions between two fluorine groups, although other factors may also be involved.⁵⁵ As has been noted in numerous structures there is a multitude of C—F...F—C interactions: type I interactions between the CF₃ groups (d_{F...F} = 2.888 Å, ∠C—F...F = 116°), and bifurcated “three-point interactions” (d_{F...F} = 2.869 and 2.874 Å; ∠F...F...F = 100°) are present between the ponytails.

Whilst DFT and AIM have been utilized to understand these weak interactions, this can be rather time-consuming. A different methodology to quantify intermolecular interactions is using Hirschfeld surfaces.⁵⁶

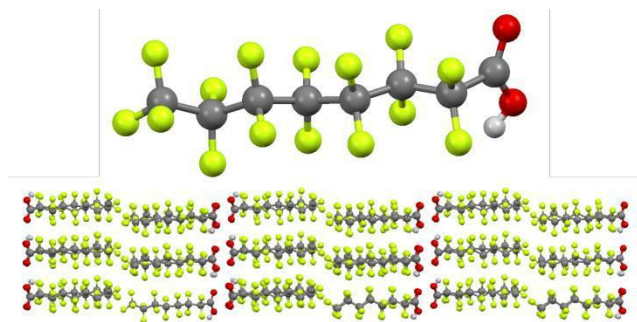


Figure 1. X-ray structure of PFOA (top) and packing as viewed along the crystallographic *b*-axis (bottom).

Surprisingly this has rarely been used in the analysis of fluorine interactions⁵⁷ so we have employed this approach to look at the interactions in a series of three carboxylic acids that have been structurally characterized by us, *viz.*

$\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CO}_2\text{H}$,^{33a} $\text{CF}_3(\text{CF}_2)_5\text{CHMeCO}_2\text{H}$ ^{32c} and $\text{CF}_3(\text{CF}_2)_6\text{CO}_2\text{H}$ and the corresponding non-fluorous octanoic acid.⁵⁸ The results of this analysis are shown in Figure 2 and more detailed plots can be found in the supporting information (Figs S17-S20). Mapping the d_{norm} parameter onto the Hirshfeld surface has been shown to give much subtle information on weak interactions and C—F...F—C interactions are clearly observed as red spots, along with the expected hydrogen bonding in the carboxylic acid functions. Also obvious in this analysis are the bifurcated F...F interactions, most notably in Figure 2(c).

Analysis of the 2D fingerprint plots yields the quantitative analysis shown in Figure 2. The C—F...F—C interactions in

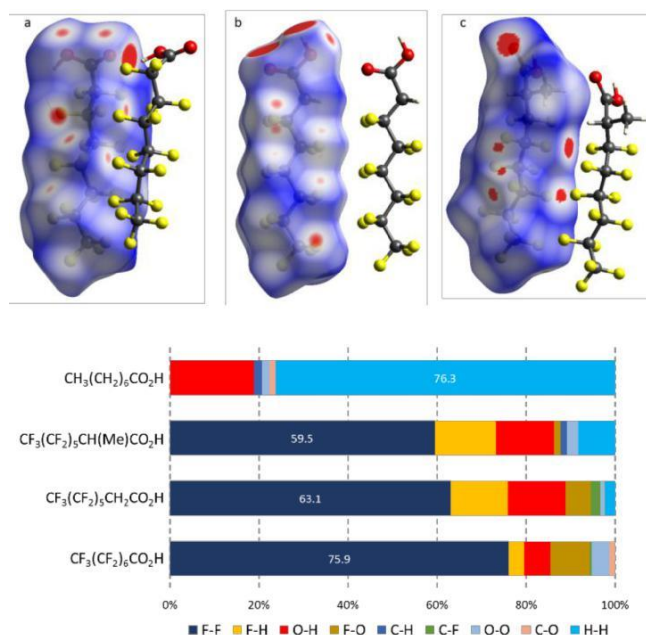


Figure 2. Map of the property d_{norm} onto Hirshfeld surfaces of (a) PFOA, (b) $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CO}_2\text{H}$ and (c) $\text{CF}_3(\text{CF}_2)_5\text{CH(Me)CO}_2\text{H}$. (plotted at -0.1-1.0) and the corresponding quantitative analysis, including octanoic acid.

PFOA is, as expected, the greatest but examination of the other acids show that the major differences are in the C—H...H—C interactions. It is perhaps coincidental that the F...F interactions in PFOA are essentially identical to the H...H interactions in octanoic acid, but work is ongoing in our group to fully explore this. However it is interesting to compare the melting points of PFOA (58.4 °C from TGA measurements, Figure S21) and octanoic acid (16-17 °C).

(b) Extraction of PFOA from water using 5, 6 and 8. Given that PFOA is a widespread persistent organic pollutant, our first aim was to find a system that would allow the removal of PFOA from water. The hosts have solubility in common

organic solvents, but we also measured the partition coefficient of PFOA between a number of common organic solvents and water;⁵⁹ interestingly at higher concentrations of PFOA foaming and the formation of a third phase was observed. The results are shown in Table S1. Inspection of the partition coefficients suggests that most solvents could act as a co-extractant, but under our experimental conditions they did not extract PFOA into the organic phase without the addition of the ligand. Screening of the solvents showed that the amphiphilic 1,3-bistrifluoromethbenzene had the greatest extraction ability, so we have chosen this for more detailed studies. It should be noted that this solvent would not be useful for large scale applications and some ligand redesign is necessary. Work is ongoing in our group to improve the large scale applicability of this idea, and will be reported on in due course. The extraction of PFOA from water into the fluorine solvent was monitored by UV-vis spectroscopy, as PFOA has an absorption band at 206 nm in water.⁶⁰ The results of the extraction with the three hosts are shown in Figure 3. It can be seen that the removal of PFOA from water is effective for all hosts, with the more rigid full cone conformer **5** the most effective. The host **8** is the slowest at extracting, suggesting that conformational rigidity might be a key factor; the shape of the curve also suggests that an intermediate is formed. UV-vis

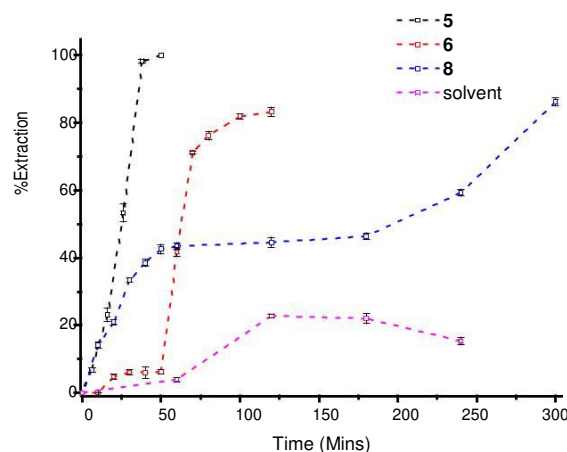


Figure 3. Results of the extraction of PFOA from water using 1 equivalent of the hosts in 1,3-(CF_3)₂ C_6H_4 , as monitored by UV-vis spectroscopy.

and ^{19}F NMR spectroscopy for host **5** shows that no PFOA is detectable in the aqueous phase at the end of the experiment. Whilst these results are pleasing, it is also worth noting that the PFOA does slowly leach back into the water phase if these phases are contacted overnight. The implications from these results are that the host-guest complex is not very stable over long periods of time. This could be due to the stronger hydrogen bonding in water over the hydrogen bonding system in the hosts.

(c) PFOA interactions with Hosts 5, 6 and 8. In order to understand the host-guest species present during the extraction, we have carried out a number of experiments to determine the stoichiometry and probe the nature of the bonding. These conclusions have been supported by computational investigations.

(i) Determination of the stoichiometry. In order to determine the number of PFOA guests that fit into the hosts **5**, **6** and **8** we have utilized a simple acid-base titration and two solution based methods, namely absorbance spectroscopy *via* a continuous variations plot⁶¹ and ^1H and ^{19}F NMR titration experiments.⁶² For the host **5**, free PFOA is only detected by titration with 0.010 M NaOH after the addition of 2 equivalents of PFOA, suggesting a 1:1 stoichiometry. Continuous variations plots confirm this stoichiometry (Figure 4). Finally analysis of the ^1H and ^{19}F NMR titrations using WINEQNMR2⁶³ gave the best fit to a 1:1 complex with a $\log\beta = 2.66 \pm 0.35$ from the ^1H NMR data. Host **6** also displays a 1:1 stoichiometry from titration and continuous variations plots and the ^1H NMR titration gives a $\log\beta = 1.90 \pm 0.21$ ($\log\beta = 1.14 \pm 0.20$ from ^{19}F NMR titrations). Given that the major difference between **5** and **6** is the reduced number of fluororous ponytails, and a smaller fluorophilic cavity in **6**, the trends in the binding constant can be readily rationalized. Host **8** is more complex as a higher stoichiometry species of ~ 6 appears to be favored from the continuous variations plot. The binding constants are, however, lower than those reported in the literature for cyclodextrin ($K_1 = 7 \times 10^4 \text{ M}^{-1}$; $K_2 = 9 \times 10^2 \text{ M}^{-2}$).⁴⁷

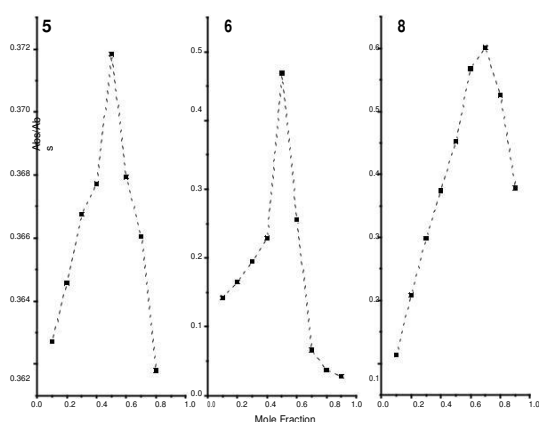


Figure 4. Plots of the continuous Variations method for hosts **5**, **6** and **8** with PFOA.

(ii) Characterization of the host-guest complexes. Given the stoichiometric ratios determined from the experiments described above, we sought to use standard characterization methods to explore the formation of these species, and any intermediates that could be formed. Thermal methods are useful in the characterization of host-guest complexes.

DSC and TGA measurements were carried out on the hosts and the 1:1 and 2:1 compounds. In our hands PFOA shows two endothermic transitions at 60 °C, ascribed to melting and 170 °C associated with vaporization (Figure S21). DSC thermograms show the loss of thermal transitions associated to the PFOA guest but no other phase transitions in the hosts **5** and **6** and **8** (Figure S22-S24); only a small increase in the thermal stability of the ligand is observed. TGA adds further weight to the proposition of an inclusion complex with the same small increase in thermal stability of the ligands observed. A plot of the derivative weight % vs temperature shows evidence of the vaporization of the guest at 197 °C for host **8**, along with decomposition of the ligand at 225 °C (Figure 5). The behavior of **6** and **7** are essentially the same and shown in Figure S25-S29; this thermal behavior is similar to that observed where β -cyclodextrin is the host.⁴⁵ The infrared spectrum of the host-guest complexes from complex **5** is shown in Figure 6 and that for **6** are shown in Figure S30. A number of points warrant discussion. Firstly the host is likely to have strong intramolecular C=O...H—N hydrogen bonding between the chains, as observed in the non-fluorous analogue (amide I band at 1654 cm^{-1} and amide II band at 1545 cm^{-1}) and the shifts in **5** are comparable.⁶⁴ The OH stretching frequency of the guest shifts to lower wavenumbers upon addition of one equivalent of PFOA and does not change in position after more equivalents, consistent with the 1:1 stoichiometry determined in solution. The C=O stretching frequencies of **5** (1667 cm^{-1} ; amide I band) and PFOA (1692 cm^{-1}) broaden but only shift slightly upon addition of 1 equivalent of PFOA (1643 cm^{-1}) and shift to slightly higher wavenumbers upon addition of 2 equivalents of PFOA (1659 cm^{-1}), whilst the amide II band (1547 cm^{-1}) is not affected.

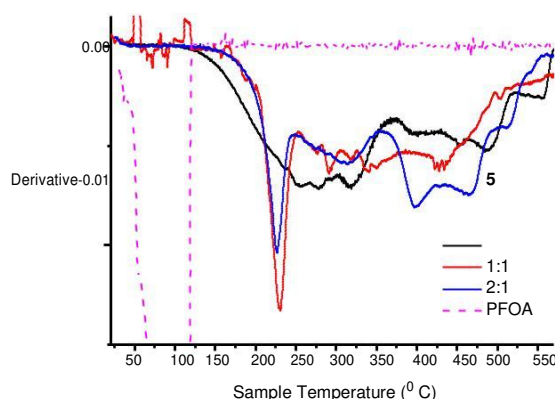


Figure 5. Derivative weight TGA of **5** and the 1:1 and 2:1 inclusion complexes.

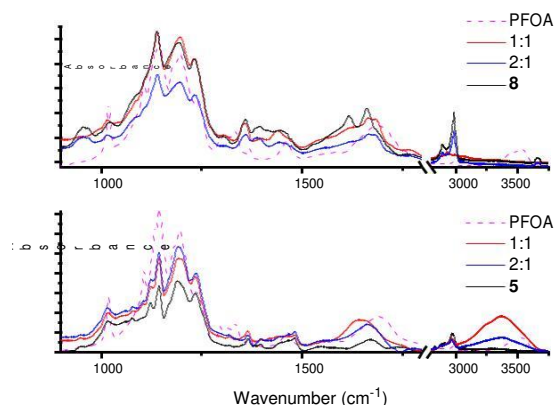


Figure 6. Infrared spectra of PFOA, 1:1, 2:1 inclusion complexes and hosts **5** (bottom) and **8** (top).

The infrared spectra of **8** and the corresponding 1:1 and 2:1 complexes are shown in Figure 6 and follow a different trend. The band at 1613 cm^{-1} does not change in position but now appears almost as a shoulder but the band at 1661 cm^{-1} shifts to 1666 in the 1:1 and 2:1 complexes and the band at 1691 cm^{-1} shifts to 1681 cm^{-1} ; the amide II bands are not affected. This is consistent with the host acting as a hydrogen bond acceptor. Interestingly the OH peak is not observable in the IR spectra of the **8**:guest complexes, but the infrared spectra do not support a proton transfer mechanism, as the ionized carboxylate show

a C=O stretch at $\sim 1650\text{ cm}^{-1}$. Conductivity measurements show that solutions of **8** and PFOA are non-conductive. Therefore the thermal characterization methods and infrared spectroscopy support the stoichiometry developed above that both **5** and **6** are 1:1 host-guest complexes whilst **8** is more complex. Moreover the hydrogen bonding network in hosts **5** and **6** do not appear to be significantly disrupted upon addition of the guest, indicating either weak binding or a different mechanism.

Solution Phase NMR Spectroscopy. Multinuclear NMR spectroscopy has been used to explore the solution conformers of the hosts and the Spin-Lattice relaxation (T_1) measurements shed further light on the inclusion complexes. DOSY NMR techniques have been increasingly utilized in supramolecular host-guest complexes,⁶⁵ and are also used. As shown in the NMR titration experiments (Figure S31-46), there is a shift of the CF_2CH_2 fluorine nucleus on the host ($\delta_F \approx -118\text{ ppm}$) and the $\text{CF}_2\text{CO}_2\text{H}$ fluorine nucleus on the guest ($\delta_F \approx -120\text{ ppm}$) which is diagnostic of an inclusion complex; the other peaks in the ^{19}F NMR spectrum are not significantly shifted. The ^1H NMR spectra are also informative as the OH peak of the guest shifts upon encapsulation. ^{19}F DOSY spectra of the host, guest and the 1:1 and 2:1 complexes have been measured and the diffusion coefficient, D_{CT} , recorded in Table 1 (selected spectra are shown in Figure 7; others are in Figure S47-50); for our measurements we have used D_{CT} for the CF_3 groups at $\delta_F = -81\text{ ppm}$, although we note that D_{CT} for the CH_2CF_2 nuclei are slightly different.

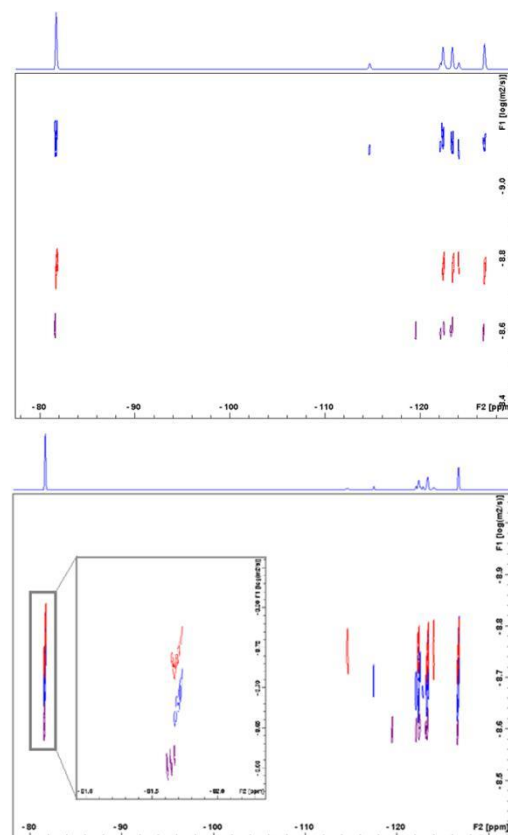


Figure 7. Overlaid ^{19}F DOSY spectra of **5**:1PFOA (top) and **6**:1PFOA (bottom) in d_6 -acetone at 300 K (Red = host; Purple = PFOA; Blue = 1:1 host-guest complex).

From this the hydrodynamic radius can be calculated via the Stokes-Einstein equation; in our examples the molecules are likely to be more prolate than spherical, so we have used the modified Stokes-Einstein equation where $n = 4$. Interestingly the hydrodynamic radius of **5** and **6** are similar, but the $1\text{D } ^1\text{H}$ NMR spectra confirm the asymmetric nature of host **6**, and variable temperature ^1H and ^{19}F NMR spectroscopy show no sign of conformational isomerization as expected.

Host **8** is the most conformationally labile, but the small hydrodynamic radius suggests that intramolecular hydrogen bonding holds this host in a relatively rigid C_3 symmetry. From the ^{19}F DOSY spectra of the host-guest complexes, there is an increase in the size of **5** with the guest whilst small changes are observed in **6**. However the small changes in D_{CT} and the corresponding hydrodynamic radius of hosts **5** and **6** support the formation of a compact inclusion complex. In contrast, host **8** has a large hydrodynamic radius, suggesting that it does not have a C_3 rigid structure in solution. Upon addition of one equivalent of guest, the hydrodynamic radius significantly shrinks indicating a conformational change to encapsulate the guest. A further addition of a guest forces a much larger structure. T_1 measurements of the individual ^{19}F nuclei were also measured as there are unique ^{19}F signals to the host ($\delta_F \approx -118\text{ ppm}$) and guest ($\delta_F \approx -120\text{ ppm}$);⁶⁶ the data is recorded in Table 1. The fluorine nuclei of the host and guest decreases

Table 1. Diffusion Coefficient, calculated hydrodynamic radius and T_1 for selected fluorous nuclei in host and 1:1 and 2:1 host:guest complexes in d_6 -acetone at 300 K.

Host	D_{CT} (ms^2)	a_H (nm)	Host CF_2^α (s)	Host CF_3 (s)	Guest CF_2^α (s)	Guest CF_3 (s)
PFOA	2.51×10^{-9}	0.43	-	-	0.30 ± 0.007	2.37 ± 0.04
5	1.60×10^{-9}	0.67	0.47 ± 0.02	1.70 ± 0.03	-	-
5:1PFOA	1.29×10^{-9}	0.83	0.09 ± 0.05	1.54 ± 0.03	0.65 ± 0.04	1.45 ± 0.05
6	1.86×10^{-9}	0.58	0.65 ± 0.05	2.02 ± 0.05	-	-
6:1PFOA	2.10×10^{-9}	0.51	0.62 ± 0.05	1.91 ± 0.3	0.69 ± 0.04	1.86 ± 0.04
8	2.13×10^{-9}	5.1	1.56 ± 0.05	1.71 ± 0.08	-	-
8:1PFOA	1.35×10^{-9}	0.79	0.71 ± 0.07	1.75 ± 0.06	0.87 ± 0.03	1.62 ± 0.05
8:2PFOA	4.85×10^{-10}	22.2	0.97 ± 0.3	1.60 ± 0.05	0.69 ± 0.12	1.6 ± 0.05

throughout the series, indicative of reduced motion, apart from the T_1 of the host CF_2 in **5**. Therefore both 1D & DOSY NMR spectroscopy and T_1 measurements indicates the formation of a host-guest complex that is stable in solution.

Solid State NMR Spectroscopy. To further probe the solid-state structures of the inclusion complexes we have utilized ^{13}C and ^{19}F solid-state MAS NMR spectroscopy and CP-MAS spectroscopy. The ^{13}C and ^{19}F NMR spectra for the guest are relatively sharp and consistent with previous results (Fig S51-S52).⁴⁵ The hosts show spectra that are relatively broad but can be assigned on the basis of their solution NMR spectra (Figures S53-S68). Variable spin rate ^{19}F MAS NMR spectroscopy are essentially identical at all spin rates, indicating that there is only one phase present (Figure S69-S71). In the MAS $^{13}C\{^1H\}$ NMR spectra of the hosts the amide carbon can be clearly observed at 169 ppm in both **5** and **6**, whilst the carbons of the fluorous chain resonate at ~127 ppm. Finally the t butyl peaks are observed at 30 ppm, but there is a shoulder at 37 ppm due to the CH_2O and $CH_2CH_2CF_2$ carbons. The $^{19}F\{^{13}C\}$ MAS NMR spectra are well resolved but rather broad and suggests slow dynamics in the fluorous chain; deconvolution of the CF_3 peak using Gaussian functions (Figure

sharpened in the host:guest complex, whilst the guest C=O resonance is likely to overlap with the host C=O amide resonance. In the $^{19}F\{^{13}C\}$ MAS NMR spectrum of this 1:1 complex the only discernible difference is in the linewidths and position of the CF_3 group at ~ -81 ppm; these could be deconvoluted (Figure 8) to give two components at $\delta_F = -81.43$ ppm (Peak 1, relative area = 0.52) and -81.64 ppm (Peak 2, relative area = 1). Whilst it is not possible to fully assign these peaks, it is clear that there are multiple CF_3 environments in the host that are reduced in the host:guest complex, possibly due to the reorganization of the fluorous cavity to accommodate the guest. The linewidths are narrower in the complex than the free host indicating an increase in dynamic behavior, at least of this group. For the 1:1 complex with host **6** the same spectral features are observed (Figure S64), but the spectra are broader and in keeping with the less conformationally rigid structure of the host. However in the $^{19}F\{^{13}C\}$ MAS NMR spectrum a more pronounced shift occurs and deconvolution of the peak reveals only two components in both the host (Peak 1: $\delta_F = -81.75$ relative area = 0.96; Peak 2: $\delta_F = -82.06$ relative area = 1) and host:guest complex (Peak 1: $\delta_F = -83.23$ relative area = 0.73; Peak 2: $\delta_F = -82.75$, relative area = 1).

8) shows three peaks at $\delta_F = -81.26$ ppm (Peak 1, relative area = 0.40), -81.64 ppm (Peak 2, relative area = 1) and -81.92 ppm (Peak 3, relative area = 0.62). The 1:1 host guest complex of **5**

was examined and whilst the $^{13}C\{^1H\}$ spectrum is generally very similar to the host, the shoulder at 37 ppm is more pronounced, or alternatively the t butyl resonance has

The linewidths increase in this complex compared to the host, indicating that there is a different dynamic mechanism to the complex formed from host **5**. Further evidence of support for this hypothesis comes from inspection of the ^{19}F $T_{1\rho}$ relaxation times of the CF_3 ($\delta_F \sim -82$ ppm), CF_3CF_2 ($\delta_F \sim -126$ ppm), CH_2CF_2 ($\delta_F \sim -113$

ppm) and the remaining CF₂ groups ($\delta_F \sim -122$ ppm), which are listed in Table 2. The CF₃ T_{1ρ} reduces slightly in the host:guest complexes of **5** and **8** but there is a very large decrease in the CF₂CH₂ group. This could possibly be due to the more constrained arrangement of the latter in the host:guest complex whereas the CF₃ group is relatively free to rotate. This has been confirmed by the variable temperature studies on **5**:1 PFOA, which show that only the CF₃ group is influenced by increasing the temperature (Figure S73).

¹⁹F → ¹³C CP/MAS NMR Spectroscopy. Polarization transfer techniques are useful for determining inclusion complexes as dipolar interactions between the host and guest can be probed directly. Thus we have measured the CP MAS spectra of the host, guests and the corresponding complexes in order to probe the orientation of the guest. The CP/MAS NMR spectra of PFOA shows magnetization transfer to the C=O resonance at 162 ppm as well as the CF carbon atoms (Figure S73). Host **5** shows the presence of a resonance at 35 ppm after a contact time of 2 ms (Figure 9) and increases in intensity with increasing contact time. This indicates that there is magnetization transfer to the CH₂O or CH₂CH₂CF₂ groups. Using the computationally derived structure (*vide infra*) this is likely to be the latter due to the strong hydrogen bonding between the amides of two chains, and consistent with the infrared data.

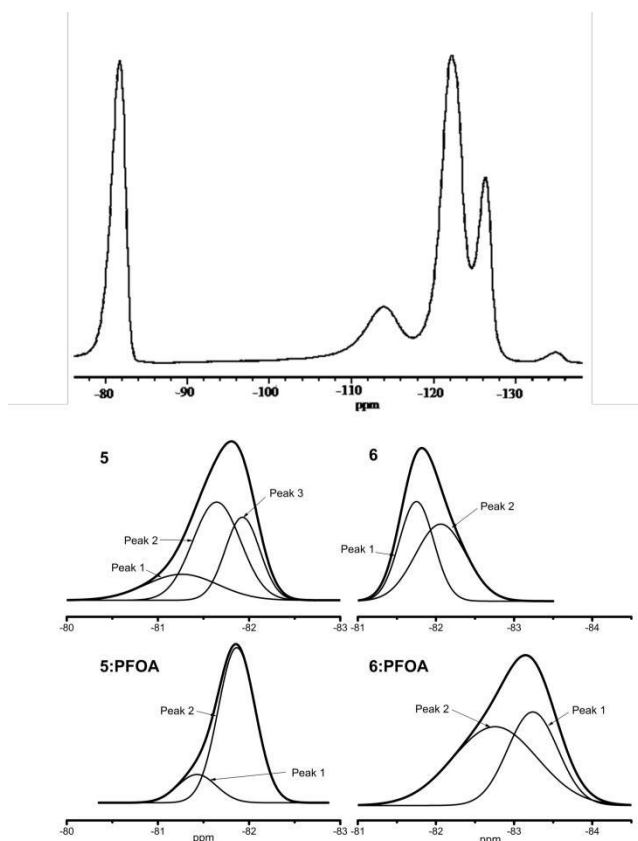


Figure 8. Top: full ¹⁹F(¹³C) MAS NMR spectrum of **5**:PFOA at 20 kHz spin rate and 298 K; Bottom: Deconvolution analysis of the spectra of the CF₃ groups of the host and host:guest complexes.

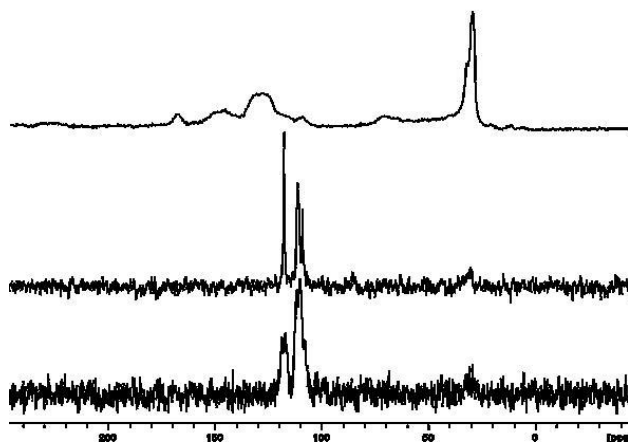


Figure 9. ¹³C{¹H} MAS NMR spectrum of **5** at 10 kHz spin rate and 298 K (Top); **5**:PFOA ¹⁹F → ¹³C CP/MAS NMR spectrum with a contact time = 10 ms (middle); **5** ¹⁹F → ¹³C CP/MAS NMR spectrum with a contact time = 2 ms (bottom).

Table 2. ¹⁹F T_{1ρ} relaxation times (ms) of the various fluororous groups in the host and host:guest complexes.

Complex	CF ₃	CF ₃ CF ₂	CF ₂	CF ₂ CH ₂
PFOA	287 ± 1.3	260 ± 2.5	223 ± 1.5	219 ± 7.9
5	178 ± 0.6	10.1 ± 0.02	11.1 ± 0.02	403 ± 2.6
5 :PFOA	155 ± 82	22 ± 0.18	8.1 ± 0.06	5.1 ± 3
6	36 ± 7.8	24 ± 0.83	24 ± 0.5	23 ± 2.8
6 :PFOA	42 ± 0.9	26 ± 0.05	14.9 ± 0.05	3.5 ± 0.009
8	8 ± 0.39	5.1 ± 1.4	5 ± 1.4	584 ± 1.4
8 :2PFOA	29.6 ± 3	18 ± 0.3	174 ± 0.2	20 ± 2.2

The same resonance is observed in the host:guest complex but longer contact times are required to observe the resonance (10 ms). This indicates that the chains are now further apart and the lack of resonance of the guest acid suggests that this group is not close to the hosts CF₂ groups i.e. is close to the CH₂ portion of the host. For host **6** there is no observable magnetization transfer (Figure S77) and no definitive magnetization transfer in the 1:1 complex, consistent with the less conformationally rigid structure compared to **5**. Interestingly there is magnetization transfer to the peak at ~30 ppm with a contact time of 8 ms in the 2:1 complex. For host **8**, there is no magnetization transfer observed indicating that the solid-state structure is not C₃ symmetry and the fluororous and non-fluororous domains are not close enough for magnetization transfer. Upon addition of the host, a resonance at 163 ppm is observed even at 1 ms contact time (Figure S81).

(c) Computational Studies. Despite numerous efforts we were unable to grow crystals suitable for X-ray diffraction of the hosts or the host:guest complexes. Therefore we looked at host **5** and the corresponding 1:1 host:guest complex by computational means in order to corroborate our

Experimental observations. The structure

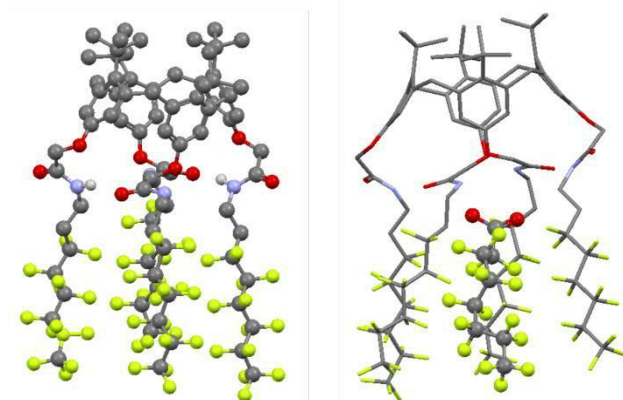


Figure 10. Computed structure of host **5** (left) and the host:guest complex (right).

of host **5** was manually built using MOE, and energy minimization followed by stochastic conformational search using the MMFF94 forcefield carried out, resulting in a cone-shaped structure (Figure 10 left) containing two short C=O...H—N hydrogen bonds ($d_{O...N}$ = 2.627 and 2.745 Å) comparable to that seen in the structure of the calixarene ligand featuring an n hexyl substituent on the amide ($d_{O...N}$ = 2.816(1) and 2.869(4) Å).⁶⁴ An extended conformations of PFOA was placed manually within the cone-shaped cavity of host **5** with the acid group in proximity to host amide groups, and the resulting complex energy minimized with MMFF94. This structure was then subjected to a short (1 ns) NVT molecular dynamics simulation to remove any artefacts of manual placement, and the final snapshot of this trajectory re-minimized. The resulting structure was optimized with molecular orbital methods, first with semi-empirical PM7 and then density functional B97-D/def2-SVP methods, both of which include empirical correction for dispersion effects, within a continuum model of aqueous solvation. This methodology treats all non-covalent interactions in the complex on an equal footing. Coordinates for the resulting prediction of a 1:1 host:guest complex of **5** with PFOA are available in Supporting Information. This structure (Figure 10 right) retains the short C=O...H—N hydrogen bonds ($O...H$ = 1.887 and 2.020 Å) within the host, as well as numerous contacts between host and guest. The most obvious of these is a hydrogen bond from O—H of PFOA to an ether oxygen of **5** ($O...H$ = 2.310 Å), but in addition there are numerous close C—H...O contacts in the range 2.4 to 2.9 Å and F...F contacts in the range 2.8 to 3.3 Å.

Atoms-in-molecules (AIM) has been utilized and there are a plethora of C—F...F—C and C—F...F—C interactions as summarized in Table 3 and typical for these type of interactions.³³ The hydrogen bonding to the ether oxygen is also reproduced. The binding energy of guest to host is calculated to be -65.16 kJ mol⁻¹ (-15.57 kcal/mol) at the DFT level after counterpoise correction indicating substantial stabilization of the host-guest complex. Clearly, a significant proportion of this stabilization stems from specific interactions noted above, but additional stabilization may stem from overall dipole-dipole interactions. DFT predicted dipole

moments for **5** and PFOA are 10.89 and 2.76 D, respectively, while that of the host-guest complex is 12.42 D indicating

Table 3. Summary of Intermolecular bond critical points.

PFOA	ρ_{bcp}	Octanoic acid	ρ_{bcp}
F...F (27)	0.009, 0.008x2, 0.007x2, 0.006x8, 0.005x5, 0.004x3, 0.003x2, 0.002, 0.001x3	H...H (1)	0.002
F...O (4)	0.008x2, 0.002x2	F...O (4)	0.008x2, 0.006x2
H...F (4)	0.008, 0.005, 0.004, 0.003	F...H (26)	0.010, 0.009x2, 0.008, 0.007x5, 0.006x3, 0.005, 0.004x2, 0.003x3, 0.002x5, 0.001
H...O (5)	0.013, 0.011, 0.008, 0.006, 0.005	H...O (5)	0.013, 0.010x3, 0.006
O...H (1)	0.011	O...H (1)	0.007

parallel alignment of dipoles in the complex, and consistent with our design principle of dipole engineering. Repeating this process with octanoic acid (OA) as the guest results in a broadly similar structure, with two C=O...H—N hydrogen bonds (1.927 and 2.085 Å) within the receptor and one O—H...O

(2.490 Å) H-bond from OA to ether oxygen in **5**. In addition, several C—H...O contacts (2.4 to 2.7 Å) are present, as well as “close” C—H...F contacts (2.4 to 2.9 Å). AIM analysis again shows an abundance of non-covalent interactions; the interactions are dominated by C—F...H—C but the hydrogen bonding interaction is the same magnitude as for PFOA. In keeping with this, the calculated binding energy of octanoic acid is only very slightly less than that for PFOA at -63.73 kJ mol⁻¹ (-15.23 kcal/mol).

(d) Reactions with other guests. Given that the calculations suggest that the host:guest binding is through the ether oxygen and C—H...O interactions, we have examined the binding energies of octanoic acid with **5** and a fluorinated guest with no capacity for hydrogen bonding to corroborate these

theories. We have only looked at ¹H and ¹⁹F NMR titrations to measure the binding constants. Octanoic acid showed no

changes in the ¹H or ¹⁹F NMR spectrum, indicating that a stable inclusion complex is not formed. Given the theory suggests that once in the cavity it should form a stable hydrogen bonded system, we ascribe this inconsistency to the fact that **5** has an intentionally designed fluorophilic cavity so the octanoic acid does not enter this cavity in solution. Using {CF₃(CF₂)₅CH₂CH₂}₂ we were able to ascertain the extent of the fluorophilic cavity without the primary hydrogen bonding.

Again no shifts in the ¹H and ¹⁹F NMR spectra were observed upon addition of up to 20 equivalents. These two experiments

show the design features worked as we anticipated and suggests selectivity for a fluorinated hydrogen bond donor/acceptor, although we have not explored this in detail. Calixarenes are known to be emissive⁶⁷ so in principle this spectroscopic technique could be utilised as a detection method. However the introduction of the fluororous ponytail in **5** and **6** quenches this emission.

Conclusions

In summary, we have designed a series of hosts for the removal of a major global pollutant utilizing hydrogen bonding and a fluorophilic cavity, excellent extraction ability observed. The drawback is the leaching of the host out of the guest over time. The stoichiometry of the host-guest complexes have been determined and fully characterized by extensive solution and solid-state NMR spectroscopic techniques. For the calix[4]arene hosts the stoichiometry is 1:1 and the binding constant is lower in the partial cone compared to the full cone, due to the reduction in the fluorophilic cavity. The conformationally labile tren based ligand is not as effective at extracting PFOA and the stoichiometry is ~ 6 indicating that a stable host:guest species is not formed; this is corroborated by the solution DOSY experiments where large hydrodynamic radii are measured for the 2:1 complex. Solid state NMR spectroscopy, particularly cross-polarization techniques, has also been used and substantiates the solution data. A computational study lends support to the experimental observations and allows us to identify the major hydrogen bonding interactions in the full cone. These have been experimentally probed by the investigation of other guests and the fluorophilic cavity and the hydrogen bond ability of the hosts appears to be important for the formation of the inclusion complex with PFOA. We have also, for the first time, reported the crystal structure of perfluorooctanoic acid.

Acknowledgements

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